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Front Cover:
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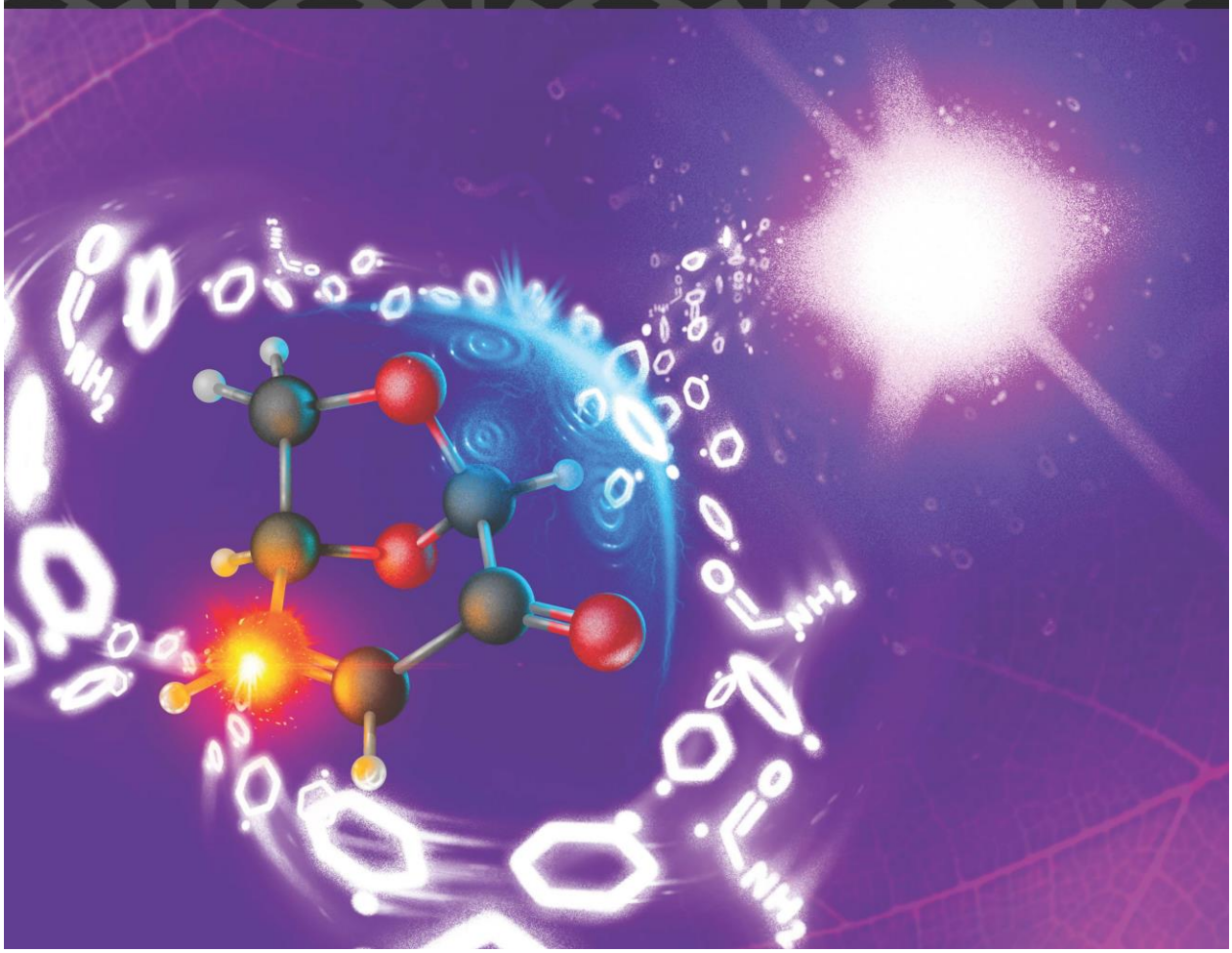

Photocatalytic Radical Addition to Levoglucosenone

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Abstract

Using photocatalysis with tetra-n-butylammonium decatungstate (TBADT), alkanes, cyclic acetals, cyclic ethers, formamide and aldehydes were added in a stereoselective way to levoglucosenone (LGO). A hydrogen atom is transferred from the donor compound to the photochemically excited TBADT, and the resulting radicals add onto LGO in a stereoselective way. In the case of the addition of adamantane, two regioisomers were obtained which form a crystalline solid solution. Cyrene™, obtained by hydrogenation of LGO, was added under the same conditions. In this case, only two of 32 possible isomers of the resulting Cyrene™ dimer were formed. The regio-selectivity of the HAT step is discussed in detail. For this purpose, bond dissociation energies and partial charges have been calculated. Transition state calculations of the radical addition to LGO explain the stereospecificity of this reaction step.

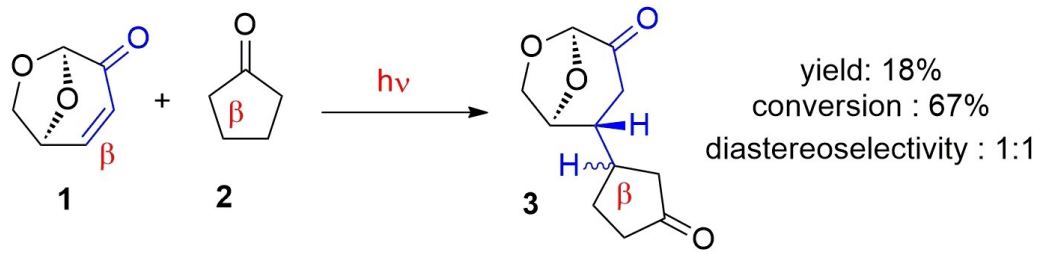
Introduction

Chemical transformation of biomass is an interesting renewable source of platform chemicals for the chemical industry.[1] These products represent an alternative to compounds obtained from fossil resources. Moreover, with regards to their chemical structure, these products are novel and thus offer many additional possibilities for application in chemical industry such as the synthesis of biologically active compounds or the preparation of materials with particular properties. In this regard, levoglucosenone (LGO) is an interesting platform chemical[2] and has been used as precursor for the production of Cyrene™, a bio-based dipolar aprotic solvent.[3] Levoglucosenone (LGO or 1) is obtained by acid-catalyzed flash pyrolysis of cellulose.[4] This compound can also be used as synthon in organic synthesis.[5] Coming from the degradation of carbohydrates (chiral pool), LGO is a homo chiral compound and possesses different functional groups such as an acetal and an α,β-unsaturated ketone, it can be thus used for numerous asymmetric syntheses.[6,7] Using photochemical or photocatalytic reactions for the transformation of biomass-based compounds represents an additional contribution to sustainable chemistry.[8,9] Among the different photosensitizers or photocatalysts[10], compounds which are capable of abstracting hydrogen atoms leading to neutral radical intermediates are also sought.[11] In this context, we became interested in the photocatalyst tetra-*n*-butylammonium decatungstate (TBADT),[12] for which a large variety of photochemically induced radical additions have been carried out,[13] to implement this strategy to LGO. The latter compound is a rather complex radical acceptor

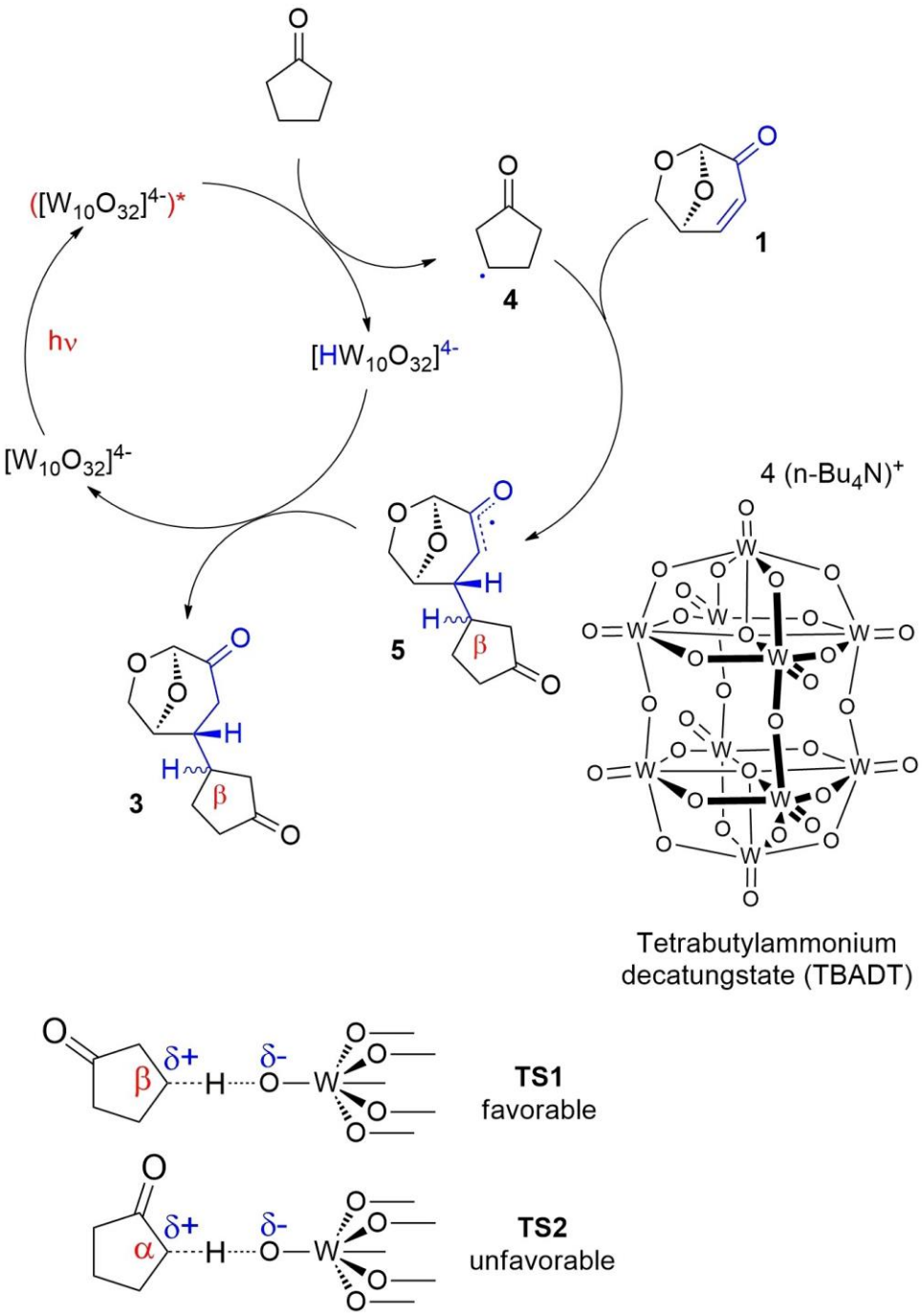
molecule. Only a few radical additions to LGO using non-photochemical conditions have been reported.[14] In previous studies, simpler acceptors such as acrylates, fumarates, vinylsulfones or acrylonitrile and derivatives, have been routinely used. These compounds are highly reactive as they are sterically unhindered or due to the presence of strong electronic effects.[15] Under photochemical conditions (irradiation around λ≈400 nm),[16] TBADT is an efficient hydrogen abstracting agent. Other photocatalysts with similar properties, such as aromatic ketones like benzophenone, could not be used as they need UV irradiation (λ<380 nm). Under these conditions, LGO undergoes efficient Norrish Type I cleavage.[17]

Results and Discussion

Recently, it was shown that the *n*-tetrabutylammonium decatungstate (TBADT)-photocatalyzed radical addition can be carried out with functionalized hydrogen atom donors.[18,19,20] Depending on electronic and steric effects of the donor compounds, a particular regioselectivity of hydrogen abstraction was observed. In this context, we decided to investigate the reaction of cyclopentanone **2** with LGO (1). The addition of **2** occurs *anti* with respect to the (-CH_2-O-) bridge in **1** (see below) and provides compound **3** (Scheme 1). However, the configuration of the chiral center generated at the cyclopentanone moiety was not controlled. According to the accepted mechanism[12,13], a hydrogen atom is transferred in the β-position of **2** to the excited TBADT yielding the radical **4** (Scheme 2). In this step, transition state TS1 is involved. Although this transition state leads to a secondary radical which is not stabilized, its formation is favored by electronic effects.[19,21,22] In the **TS1**, the more nucleophilic position matches with the electrophilic character of the excited TBADT photocatalyst while in **TS2** a corresponding mismatched combination is established. Radical **4** adds to LGO leading to the radical intermediate **5**. Reduction of the latter yields the final product and regenerates the photocatalyst.



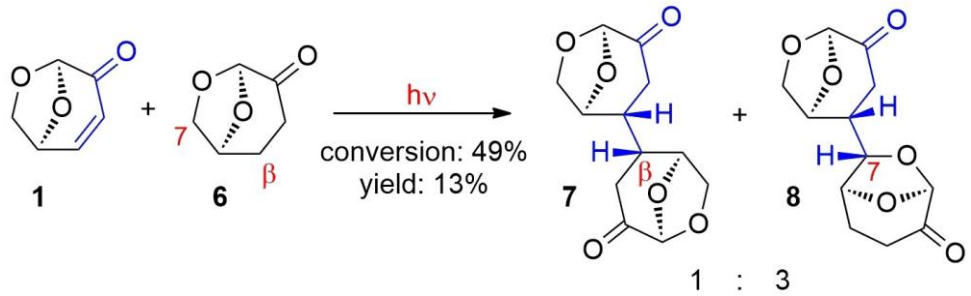
Scheme 1. Stereoselective photocatalytic radical addition of cyclopentanone **2** to LGO (1): blue LED, 5 equiv. RH, 5 mol% TBADT, MeCN, 8 h.



Scheme 2. Accepted mechanism[12,13] for the photocatalytic addition of cyclopentanone to LGO with TBADT as photocatalyst.

In order to get more insight into both the mechanistic details and the stereochemical reaction course, Cyrene™ (**6**) was added to 1 (Scheme 3). As mentioned above, **6** is obtained from **1** on industrial scale through a palladium-catalyzed hydrogenation. It is noteworthy to mention that a biotechnological process involving alkene reductase OYE 2.6 has also been developed but remains at the proof-of-concept stage.[23] Two compounds have been isolated: the C2-symmetric compound **7** resulting from hydrogen abstraction in the β position of **6** and its stereospecific addition to **1**, and compound **8** resulting from hydrogen abstraction in position 7 of **6** and the

consecutive addition of the radical species to **1**. It is worth mentioning that, in this case, the newly formed chiral center on the hydrogen donor was controlled. This result is in contrast to what was observed for the transformation with cyclopentanone (compared to Scheme 1). A COSMO analysis of Cyrene™ **6** shows the steric hindrance for creation of a chiral center in the β and 7 positions are almost identical (Figure 1).[3,24]



Scheme 3. Stereoselective photocatalytic radical addition of Cyrene™ (**6**) to LGO (**1**): blue LED, 5 equiv. RH, 5 mol% TBADT, MeCN, 8 h.

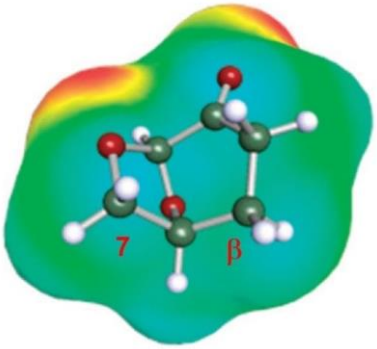


Figure 1. σ-Surface (COSMO surface) of dihydrolevoglucosenone (Cyrene) (with permission adapted from J. Sherwood, M. De bruyn, A. Constantinou, L. Moity, C. R. McElroy, T. J. Farmer, T. Duncan, W. Raverty, A. J. Hunt, J. H. Clark, *Chem. Commun.* 2014, *50*, 9650–9652 (Copyright 2014) Royal Society of Chemistry).

Only two of the five possible regio-isomers were formed,without taken into account corresponding stereoisomers. In order to get more information on this selectivity, we calculated C-H bond dissociation energies (Figure 2a) and partial charges (Figure 2b) for Cyrene™. As expected, a more stable radical (**R1**) is formed by hydrogen abstraction in the 3 position whereas radicals in positions 2 (**R2**), 1 (**R3**) and 5 (**R4**) are less stable. Compared to these three radicals, R5 possesses some stability. **R3** and **R4** are σ radicals which are generally less stable than corresponding π radicals[25] as they can be formed in positions 3, 2 and 7. The values for **R1** and **R2** reflecting thermodynamical aspects do not contribute to an explanation of the observed regioselectivity. As discussed above for the addition of cyclopentanone, partial charges at the atoms have an influence on the energy of different transition states and thus on the kinetic of the reaction.[19,21] In the case of cyrene™ (Figure 2b), almost the same value of a negative partial charge was calculated for the carbon atoms in positions 3 and 2. The increased steric hindrance for the hydrogen atom transfer from position 3, which is caused by the carbonyl function, reduces the rate of the hydrogen abstraction in this position when compared to that one in position 2. Some negative charge was also calculated for the carbon atom in position 7 which favors

hydrogen abstraction in this position and the formation of product **8**. The high selectivity of this reaction is therefore best explained by the partial charges in cyrene™.

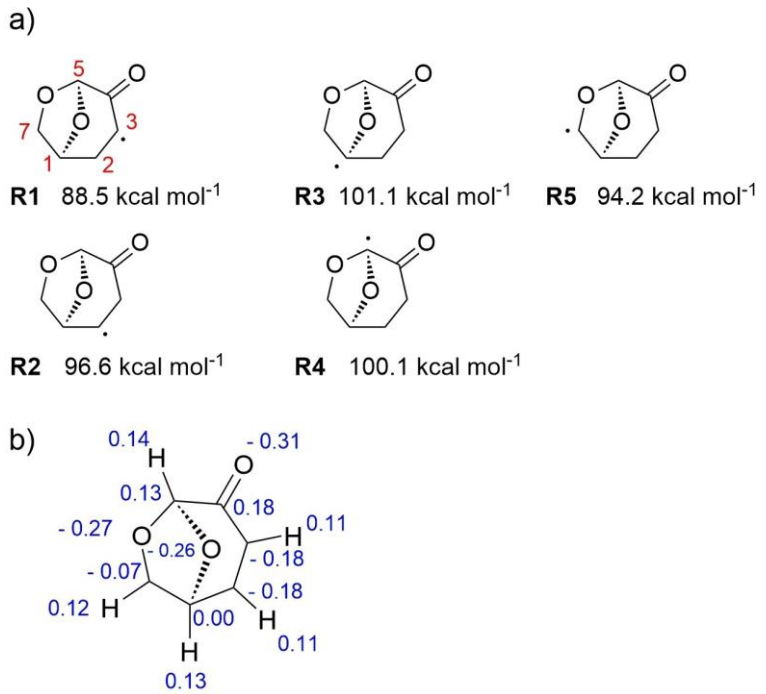
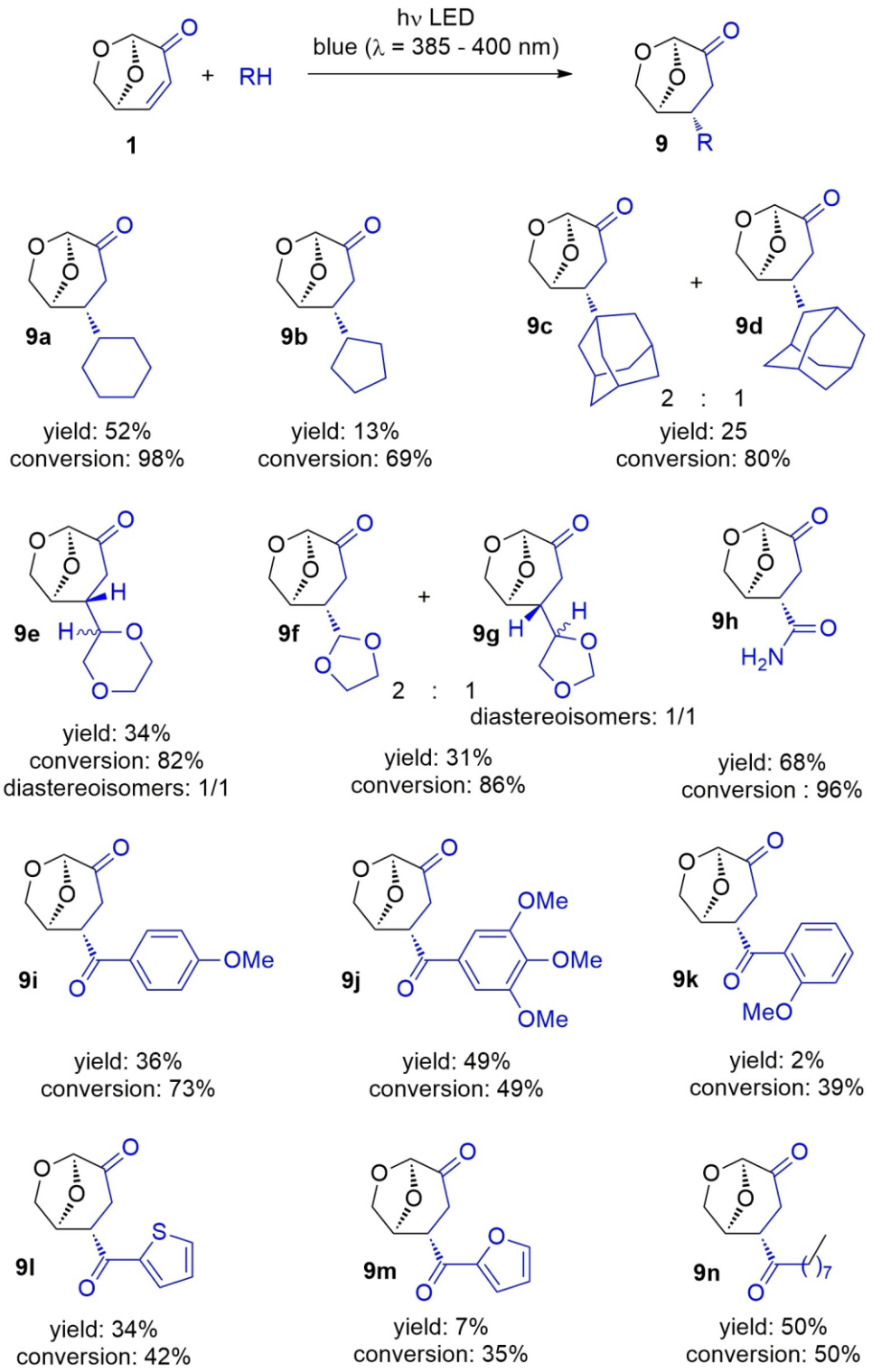


Figure 2. a) C-H bond dissociation energies (UM062X/6-311+ +G**, Thermochemistry calculations: KistHelp) for Cyrene™. b) Partial charges (UM062X/6-311+ +G**, Charges model: Atomic Dipole moment corrected atomic Charges (ADCH) (Multiwfn)) for Cyrene™.

We continued our investigation with the photocatalytic radical addition of alkanes to 1 (Scheme 4). In order to compare the different reactivities, a constant irradiation time (8 hours) was chosen and setup remained unchanged (see supporting information). A longer irradiation time didn't lead to higher conversion. Cyclohexane (**9a**) and cyclopentane (**9b**) were added, the addition of the first being more efficient. The reaction with adamantane gave two products **9c** and **9d**. Adamantane derivatives are of high interest in many domains such as medicinal chemistry.[26,27] The first product resulted from hydrogen abstraction at the carbon atom in position 1 while **9d** was formed through C-H bond cleavage at the CH_2 moiety (position 2) of the adamantane. This result is in line with very similar C-H bond dissociation energies for both positions.[26,28] In all cases, the addition was stereospecific and the attack occurred *anti* with respect to the (-CH_2-O-) bridge in **1**. Cyclic ethers such as 1,4-dioxane were successfully added (**9e**). In this case, two stereoisomers were obtained, however the configuration of the chiral center at the dioxolane moiety was not controlled. In the reaction of dioxolane, two regioisomers **9f** and **9g** were formed. As in the case of **9e**, two diasteroisomers of compound **9g** were obtained. The addition of formamide (**9h**) was carried out in high conversion and selectivity under the chosen reaction conditions. The photocatalytic radical addition of aromatic aldehydes has also been performed. While the addition of anisaldehyde (**9i**) and gallic aldehyde (**9j**) was successful, that of salicylaldehyde (**9k**) proved unsuccessful. Heterocyclic aromatic aldehydes were also added. While the reaction with thiophene aldehyde (**9l**) was successful, the reaction with furfural (**9m**) was less efficient. The addition of nonanal (**9n**) proved efficient and opens further perspectives for the application of the reaction.



Scheme 4. Photocatalytical radical addition to levoglucosenone: blue LED, 5 equiv. RH, 5 mol% TBADT in MeCN (or MeCN/benzene: 70/30 in the case of **9c,d**), 8 h. Yields are given for isolated compounds.

All compounds resulted from an attack of the photochemically generated radicals to **1** *anti* with respect to (-CH_2-O-) bridge as it was confirmed by X-ray diffraction analysis on the respective crystals. Structures of compounds **9i** and **9m** are depicted in Figure 3.[29] This stereoselectivity is

also observed in many Michael reactions with LGO.

The separation of the adamantane adducts **9c** and **9d** was proven elusive by chromatography. Interestingly, attempt to crystallize the mixture yielded both compounds to cocrystallize.[30] The crystal was found to be disordered, forming an uncommon *solid solution*[31,32] whereby the two different compounds **9c** and **9d** occupy the same lattice site (Figure 4, middle). In the particular crystal measured, the ratio between the two compounds was found to be 2:1 (**9c** :**9d**) from the occupancy of the two different refined parts. Further crystallographic details are available in supporting information.

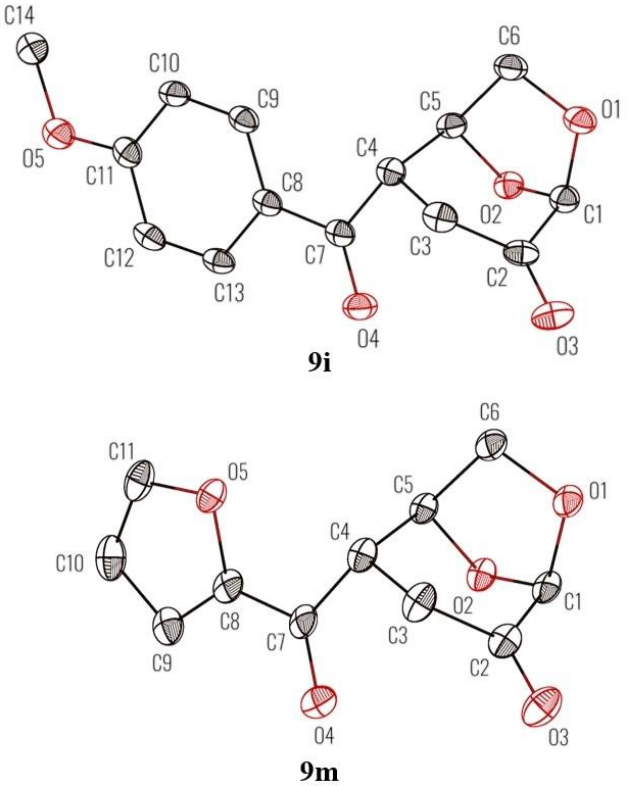


Figure 3. ORTEP diagram (drawn at 50% probability level) of the molecular structure of the photochemical adducts **9i** (top) and **9m** (bottom) obtained by X-ray diffraction analyses. H atoms have been omitted for clarity.

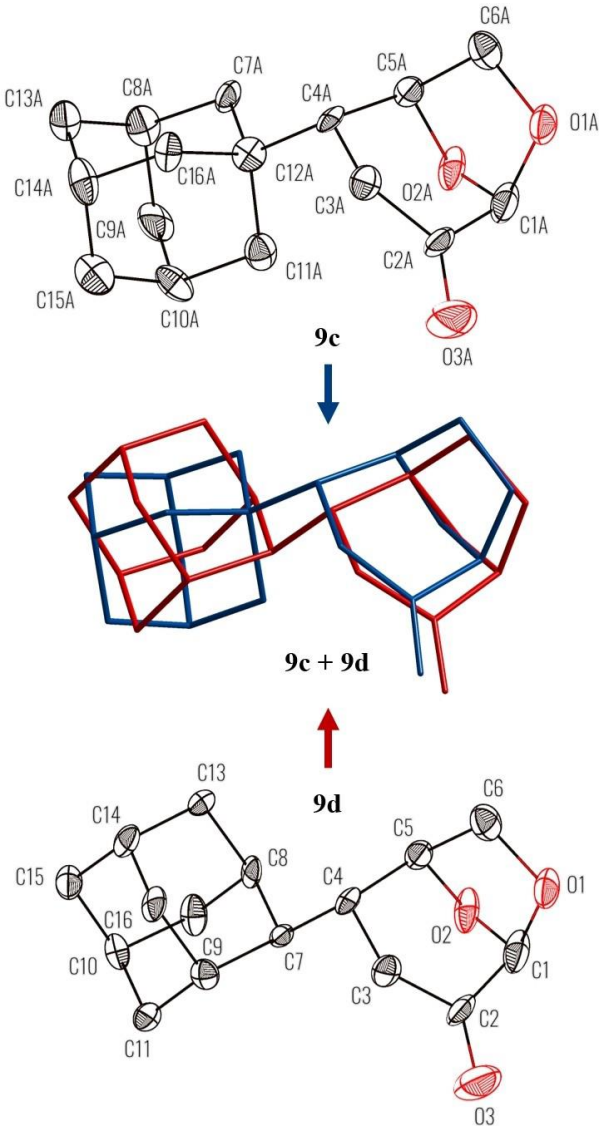


Figure 4. ORTEP diagram (drawn at 50% probability level) of the molecular structure of the photochemical adducts **9c** (top) and **9d** (bottom) obtained by X-ray diffraction analyses. The asymmetric unit of the solid solution is represented in the middle, consisting in compound **9c** (blue) and **9d** (red) occupying the same lattice site. H atoms have been omitted for clarity.

In order to explain the complete stereoselectivity of the attack of radical intermediates, we have calculated the transition state energies for the attack *syn* and *anti* with respect to the (-CH_2-O-) bridge in LGO (Figure 5) with the help of Gaussian 16 Rev. B.01 [33] and KiSThelP for thermochemical analysis.[34] In the case of the reaction with the formamidyl radical the corresponding energy difference is 4.53 kcal/mol. In the case of the reaction with cyclohexyl radicals the energy difference is 5.24 kcal/mol. Both are in favor of the *anti* attack. These energy differences for the competing formation of two diastereoisomers enables the formation of only one of them.

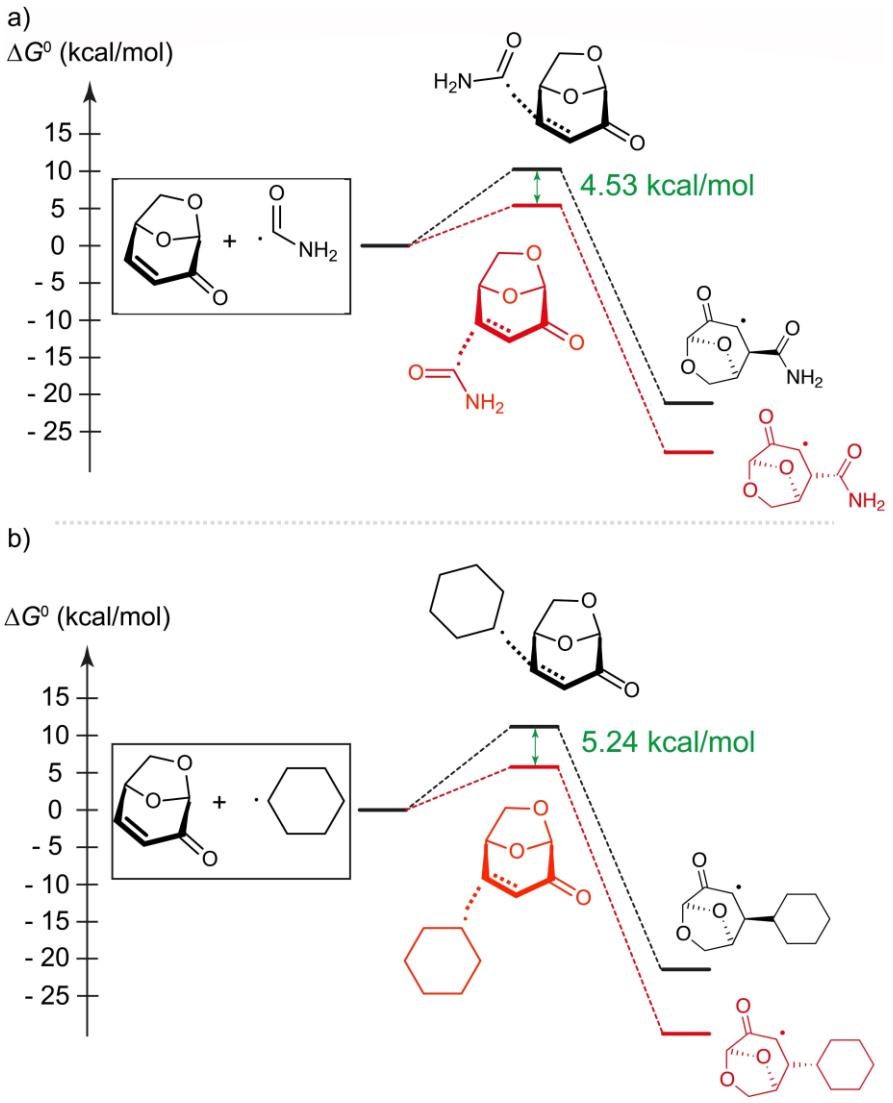


Figure 5. DFT calculation of energy differences for the diastereoselective attack of radical intermediates to LGO ((U)M062X/6-311+ +G**) at 298 K, 1 bar in acetonitrile (PCM solvation model). a) Reaction of a cyclohexyl radical, b) reaction of a formamidyl radical.

In order to decipher the radical addition stereoselectivity, Independent Gradient Model (IGM) was used to extract and visualize intermolecular interactions at the transition-state in the case of formamidyl (Figure 6a) and cyclohexyl radicals (Figure 6b). Intrinsic Bond Strength Index (IBSI) was

concomitantly calculated to evaluate the strength of the forming bond in both cases and the contribution of hydrogen-bonding to the stabilization of the transition-state in formamidyl instance.[35]

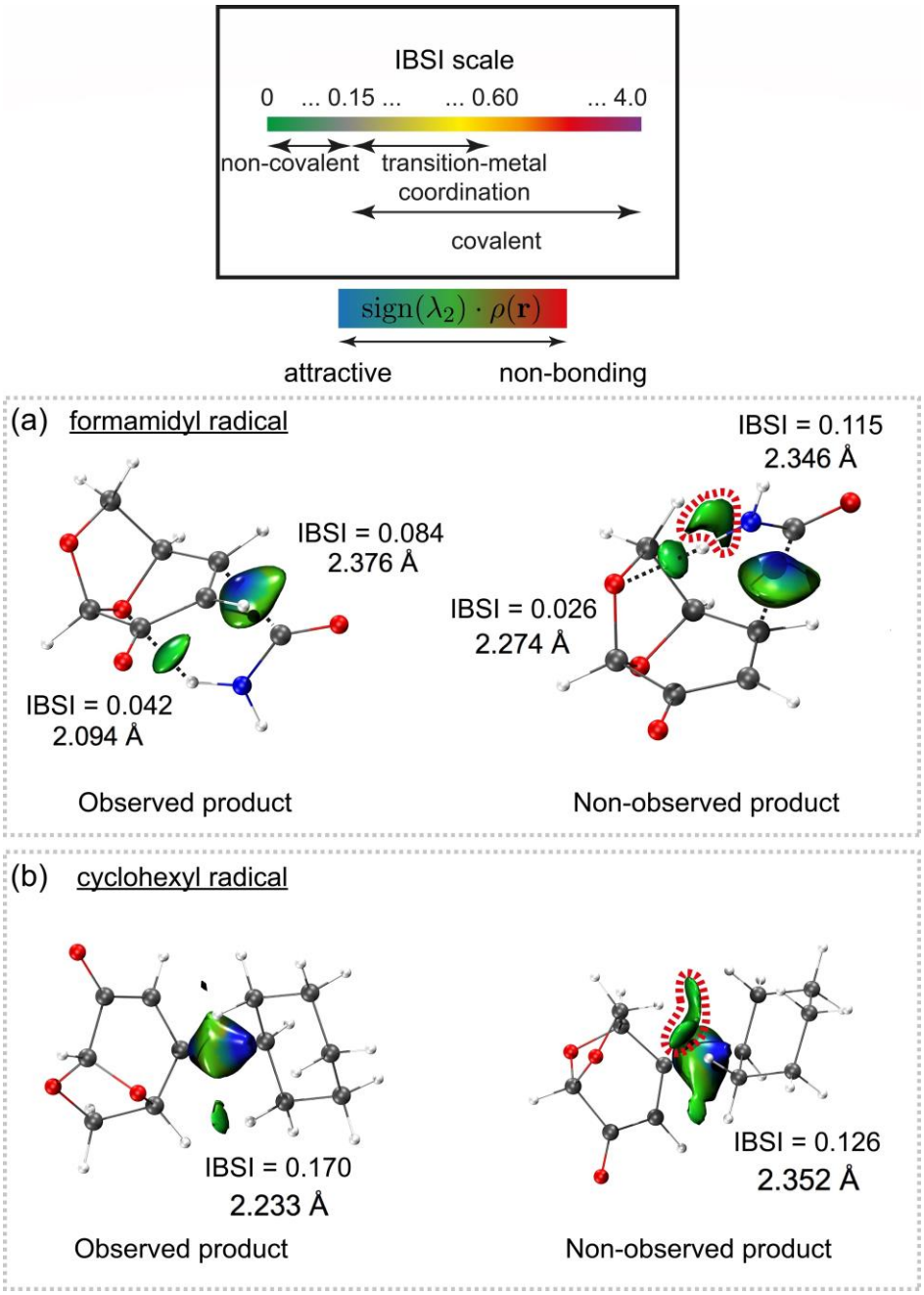


Figure 6. IGM analysis applied for the addition of the formamidyl (a) and cyclohexyl (b) radicals in the transition-state (δg=0.015 a.u.). Blue-Green-Red (BGR) color range for the attractive/non-bonding interactions: [-0.01; 0.01]. Isosurfaces of contragradience due to steric hindrance is indicated by dotted red lines.

In both cases, a zone of non-bonding behavior is detected by IGM analysis for the non-observed diastereoisomer, in contrast to the observed product. Surprisingly, IBSI shows that the hydrogen-bond between one of the hydrogen of formamidyl radical with one of the oxygen of levoglucosenone is not a major contribution towards the formation of only one diastereoisomer in the case of **9h**. The value of the former remains almost unchanged from reactants to the transition-state, from 0.042 a.u. to 0.026 a.u. Data provided by IGM analysis, in accordance with transition-state calculation, indicate that both energy differences between observed and non-observed product in formamidyl and cyclohexyl cases are close (4.53 *vs* 5.24 kcal/mol respectively, Figure 5). This enabled a profound study of these systems. 'Steric hindrance' via Natural Bond Orbital analysis[36] was performed and showed both radical addition of formamidyl and cyclohexyl radicals in the case of observed products are favored by more than 8.0 kcal/mol in the case of formamidyl and 6 kcal/mol in the case of cyclohexyl (Figure S4 and Figure S5 provided in SI). Symmetry-Adapted Perturbation Theory analysis (SAPT) via Psi4 program[37] consolidates experimental observation and theoretical study. In the case of addition of the formamidyl radical, decomposition of the intermolecular interaction energy at the transition-state showed a weak contribution of hydrogen-bond in terms of electrostatic energy in the case of the addition of formamidyl radical. However, exchange energy (Pauli repulsion), related to the physical definition of steric hindrance, is in favor of the formation of the isolated product **9h** (Table S1). Formation of product **9a** is likely to be favored by a combined contribution of electrostatic, dispersion and induction energies exceeding exchange energy (Table S2).

Conclusion

The polyoxometalate photocatalyst tetra-*n*-butylammonium decatungstate (TBADT) was used to generate radical intermediates under blue LED irradiation. A variety of these radicals have been added to the electron deficient double bond of Levoglucosenone, a biomass-derived complex chiral unsaturated compound. The radical attack of acyl and formamidyl radicals was efficiently performed. The addition occurred in a stereospecific way *anti* with respect to the (-CH_2-O-) bridge of Levoglucosenone. A high regio- and stereoselectivity of the radical addition of Cyrene™ was observed as only two of 32 possible isomers were formed. A particular regioselectivity was also observed for the addition of cyclopentanone with a radical species generated in the β position. Bond dissociation energies (thermodynamic effect) and partial charges (kinetic effect) at the radical precursors as well as steric effects determine the selectivity of the reactions.

Experimental Section

General information. Photochemical reaction has been carried out with LED IP FL-30 (eurolite). Emission spectrum is given in Figure S1 (supporting information). UV/vis spectrum of TBADT catalyst was recorded with a UVKON 941 PLUS (KONTRON Instruments) and is given in Figure S2 (supporting information). Photochemical reaction progress was followed via TLC with Kieselgel 60F254 plates from Merck. Revelations were carried out using two revelators: sulfuric acid (solution of 5% sulfuric acid (95%) in methanol) and Hannessian's stain (1.5 g of cerium

ammonium nitrate, 3.75 g of ammonium molybdate and 15 mL of sulfuric acid (95%) are dissolved in 150 mL of distilled water). Preparative chromatography was carried out with silica gel 60 A from Carlo Erba Reactifs-SDS. Specific rotations were recorded with a Model 341 polarimeter from Perkin Elmer using a Hg lamp (λ=546 nm) and calculated as follows [Eq. (1)]:

$$[\alpha]_{T=20°\mathrm{C}}^{546\ \mathrm{nm}} = \frac{100 \cdot \alpha}{l \cdot c} \qquad (1)$$

with *α* the read angle, *l* the path length in dm and *c* the concentration in g/100 mL. NMR spectra were recorded with a 500 MHz Bruker Avance Neo spectrometer equipped with a SP BB&19F/1H Iprobe (500.28 MHz for ^{1}H and 125.8 MHz for ^{13}C). Chemical shifts are given in ppm relatively to TMS using residual solvent signals as secondary references. Data for ^{1}H NMR spectra were reported as follows: chemical shift in parts per million (ppm), peak shape multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, p=quintet, hex=sextet), coupling constant in Hz and integration. The assignment of signals to isomers and diastereoisomers are based on integration of the signals in the NMR of the mixture of these latter unless otherwise indicated. High-resolution mass spectrometry (HR-MS) data were recorded using a spectrometer equipped with either electrospray ionization source (ESI), or atmospheric solids analysis probe (ASAP) or using a spectrometer equipped with electronic impact ionization source (EI) in positive mode associated with a TOF analyzer. IR spectra were recorded on a Nicolet AVATAR 320 FT-IR using KBr salt or NaCl plates. Band frequencies are given in cm^{-1}. Melting points were recorded using a Stuart Melting point apparatus SMP3. X-Ray Diffraction data were collected on a Bruker D8 VENTURE dual wavelength single-crystal X-Ray diffractometer equipped with a PHOTON II detector at 117, 120 and 130 K for **9i**, **9m** and **9c**/**9d** respectively K using Cu-Kα radiation (*λ*=1.5418 Å). The Apex3 software[38] was used for data reduction. Using Olex2,[39] the structures were solved using SHELXT[40] structure solution program using Intrinsic Phasing and refined with the SHELXL[41] refinement package using Least Squares minimization on *F2*, using all data. All non-hydrogen atoms were refined with anisotropic displacement parameters, while all hydrogen atoms were placed at geometrical estimates using the riding model.

General procedure for photocatalytic reaction. In a 100 ml round bottom flask equipped with a stirring bar is placed 1.0 equiv. of Levoglucosenone **1**, 5.0 equiv. of hydrogen-donor R-H, 0.05 equiv. of TBADT and 50 mL of acetonitrile. The solution is degassed with argon during 10 minutes under vigorous stirring. Then, the reaction mixture is irradiated with LED spots during 8 hours under stirring (typical apparatus given in Figure S3 in the supporting information). This former takes a deep blue color as a sign of the reduction of TBADT. The solvent is removed under reduced pressure and the crude product is purified over silica column gel.

(1*S*,2*R*,5*R*)-2-(3-oxocyclopentyl)-6,8-dioxabicyclo[3.2.1]octan-4- one (3). Levoglucosenone **1** (0.56 g, 4.4 mmol, 1.0 equiv.) was dissolved in 50 mL of acetonitrile with cyclopentanone (1.87 g, 1.96 mL, 5.0 equiv.) and TBADT (0.74 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: petroleum ether/ethylacetate 70/30), product **3** was isolated in 18% yield (0.17 g, 0.8 mmol as a 1/1 mixture of diastereoisomers) as a transparent oil following a conversion of 67% (0.19 g of Levoglucosenone is recovered within 8 hours of reaction). *Rf*=0.26 (petroleum

ether/ethylacetate 50/50, revelation with Hannessian's stain). ^{1}H NMR (500.28 MHz, $CDCl_3$, 300 K): δ=1.41–1.51 (m, 1 H), 1.51–1.61 (m, 1 H), 1.74–1.83 (m, 1 H), 1.83–1.92 (m, 1 H), 2.00–2.08 (m, 2 H), 2.16–2.26 (m, 3 H), 2.27–2.40 (m, 5 H), 2.40–2.51 (m, 3 H), 2.51–2.56 (m, 1 H), 2.79 (dd, *J*=16.9, 7.8 Hz, 1 H), 2.82 (dd, *J*=16.9, 7.8 Hz, 1 H), 3.99–4.06 (m, 4 H), 4.51–4.55 (m, 1 H), 4.68–4.72 (m, 1 H), 5.09 (s, 2 H). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): δ =27.9, 28.1, 34.8, 36.1, 38.4, 38.6, 38.9, 38.9, 43.4, 43.5, 47.2, 47.2, 68.0, 68.0, 74.4, 75.8, 101.7, 101.7, 199.8, 200.0, 217.2, 217.3. HRMS (TOF MS ES+): calcd for $C_{11}H_{15}O_4^{+}$ [M+H$^+$]=211.0970, found=211.0968. IR (NaCl): ~*v*=1736, 2849, 2915 cm^{-1}.

(1*S*,1'*S*,2*R*,2'*R*,5*R*,5'*R*)-6,6',8,8'-tetraoxa[2,2'-bi-(bicyclo[3.2.1]octane)]-4,4'-dione (7) and (1*S*,1'*S*,2*S*,5*R*,5'*S*,6'*S*)-6,7',8,8'-tetraoxa[2,6'-bi(bicyclo[3.2.1]octane)]-2',4-dione (8). Levoglucosenone **1** (0.58 g, 4.6 mmol, 1.0 equiv.) was dissolved in 50 mL of acetonitrile with Cyrene (2.95 g, 2.36 mL, 5.0 equiv.) and TBADT (0.76 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: petroleum ether/ethylacetate 80/20), product **7** and **8** were isolated as a 1/2.7 oil mixture of regioisomers in 13% yield (0.15 g, 0.6 mmol) following a conversion of 49% (0.3 g of Levoglucosenone is recovered within 8 hours of reaction). *Rf*=0.21 (petroleum ether/ethylacetate 70/30, revelation with Hannessian's stain). ^{1}H NMR (500.28 MHz, $CDCl_3$, 300 K): δ=2.02–2.09 (m, 2.2 H, 3 H from 7 and 1 H from 8), 2.15–2.21 (m, 2.4 H, 1 H from 7 and 2 H from 8), 2.32 (dddd, *J*=14.0, 11.3, 7.1, 3.9 Hz, 1 H, 8), 2.38–2.46 (m, 1 H, 8), 2.69 (ddd, *J*=16.7, 11.3, 8.8 Hz, 1 H, 8), 2.81–2.86 (m, 1.8 H, 2 H from 7 and 1 H from 8), 4.02–4.11 (m, 3.5 H, 4 H from 7 and 2 H from 8), 4.25 (d, *J*=10.1 Hz, 1 H, 8), 4.35–4.38 (m, 1 H, 8), 4.95–5.0 (m, 1.8 H, 2 H from 7 and 1 H from 8), 5.11 (s, 0.8 H, 7), 5.137 (s, 1 H, 8), 5.145 (s, 1 H, 8). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): δ=29.6 (8), 31.4 (8), 34.2 (8), 35.9 (7), 42.4 (7), 44.9 (8), 67.9 (7), 68.0 (8), 73.1 (8), 73.8 (7), 75.8 (8), 78.2 (8), 101.4 (8), 101.8 (7), 102.4 (8), 198.7 (8), 199.4 (7), 199.6 (8). HRMS (TOF MS ASAP+): calcd for $C_{12}H_{15}O_6^{+}$ [M+H$^+$]=255.0870, found=255.0869. IR (NaCl): ~*v*=1736, 1731, 2946, 2900 cm-$^{1.}$

(1*S*,2*R*,5*R*)-2-cyclohexyl-6,8-dioxabicyclo[3.2.1]octan-4-one (9a). Levoglucosenone **1** (0.55 g, 4.4 mmol, 1.0 equiv.) was dissolved in 50 mL of acetonitrile with cyclohexane (1.84 g, 2.36 mL, 5.0 equiv.) and TBADT (0.72 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: petroleum ether/ethylacetate gradient 95/5 to 90/10), product **9a** was isolated in 52% yield (0.49 g, 2.3 mmol) as a yellowish oil following a conversion of 98% (0.01 g of Levoglucosenone is recovered within 8 hours of reaction). *Rf*=0.44 (petroleum ether/ethylacetate 50/50, revelation with Hannessian's stain). [*α*]546 nm. *T*=20°C=-205 (*c*=0.45 in acetonitrile). ^{1}H NMR (500.28 MHz, $CDCl_3$, 300 K): δ=0.94 (qd, *J*=12.4, 3.2 Hz, 1 H), 1.04 (qd, *J*=12.4, 3.2 Hz, 1 H), 1.14 (tt, *J*=12.4, 3.4 Hz, 1 H), 1.24 (qt, *J*=12.9, 3.2 Hz, 2 H), 1.47 (tdt, *J*=11.2, 3.4 Hz, 1 H), 1.63–1.69 (m, 1 H), 1.70–1.90 (m, 5 H), 2.35 (dd, *J*=16.5, 1.6 Hz, 1 H), 2.67 (dd, *J*=16.5, 8.2 Hz, 1 H), 3.95–3.98 (m, 2 H), 4.71–4.75 (m, 1 H), 5.05 (s, 1 H). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): δ=26.3, 26.4, 26.5, 30.5, 31.0, 35.0, 40.0, 46.7, 68.5, 74.8, 101.6, 201.3. HRMS (TOF MS ASAP+): calcd for $C_{12}H_{19}O_3^{+}$ [M+H$^+$]=211.1334, found=211.1333. IR (NaCl): ~*v*=1420, 1449, 1736, 2853, 2925 cm^{-1}.

(1*S*,2*R*,5*R*)-2-cyclopentyl-6,8-dioxabicyclo[3.2.1]octan-4-one (9b). Levoglucosenone **1** (0.66 g, 5.2 mmol, 1.0 equiv.) was dissolved in 50 mL of acetonitrile with cyclopentane (1.53 g, 2.04 mL,

5.0 equiv.) and TBADT (0.87 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: petroleum ether/ethylacetate 90/10), product **9b** was isolated in 13% yield (0.14 g, 0.7 mmol) as a yellowish oil following a conversion of 69% (0.21 g of Levoglucosenone is recovered within 8 hours of reaction). *Rf*=0.62 (petroleum ether/ethylacetate 50/50, revelation with Hannessian's stain). [*α*]546 nm *T*=20°C=-110 (*c*=0.14 in acetonitrile). ^{1}H NMR (500.28 MHz, $CDCl_3$, 300 K): δ=0.95–1.16 (m, 2 H), 1.47–1.66 (m, 4 H), 1.78–1.95 (m, 3 H), 1.95–2.06 (m, 1 H), 2.25 (d, *J*=16.4 Hz, 1 H), 2.70 (dd, *J*=16.4, 7.7 Hz, 1 H), 3.90–3.97 (m, 2 H), 4.58 (s, 1 H), 5.00 (s, 1 H). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): δ=25.1, 25.2, 31.0, 31.1, 36.3, 41.5, 47.4, 68.0, 76.0, 101.5, 201.0. HRMS (TOF MS ASAP+): calcd for $C_{11}H_{17}O_3^{+}$ [M+H$^+$]=197.1178, found=197.1177. IR (NaCl): ~*v*=1736, 2868, 2959 cm^{-1}.

(1*S*,2*R*,5*R*)-2-(adamantan-1-yl)-6,8-dioxabicyclo[3.2.1]octan-4-one (9c) and **(1*S*,2*R*,5*R*)-2-(adamantan-2-yl)-6,8-dioxabicyclo[3.2.1]octan-4-one (9d).** Levoglucosenone **1** (0.51 g, 4.0 mmol, 1.0 equiv.) was dissolved in a solution of 35 mL acetonitrile and 25 mL benzene with adamantane (2.8 g, 5.0 equiv.) and TBADT (0.68 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: petroleum ether/ethylacetate 95/5), product **9c** and **9d** were isolated as a 2/1 solid mixture in 25% yield (0.27 g, 1.0 mmol) following a conversion of 80% (0.1 g of Levoglucosenone was recovered within 8 hours of reaction). *Rf*=0.29 (petroleum ether/ethylacetate 95/5, revelation with Hannessian's stain). ^{1}H NMR (500.28 MHz, $CDCl_3$, 300 K): δ= 1.52–1.60 (m, 5 H, 4 H from **9c** and 2 H from **9d**), 1.60–1.92 (m, 15 H, 10 H from **9c** and 10 H from **9d**), 1.97–2.03 (m, 3 H, 2 H from **9c** and 2 H from **9d**), 2.10 (s, 0.5 H, 1 H from **9d**), 2.27–2.34 (m, 1 H, 2 H from **9d**), 2.46–2.55 (m, 2 H, **9c**), 2.69 (dd, *J*=16.3, 7.7 Hz, 0.5 H, 1 H from **9d**), 3.87 (dd, *J*=7.2, 1.0 Hz, 1 H, **9c**), 3.94 (dd, *J*=7.2, 5.4 Hz, 1 H, **9c**), 4.00–4.07 (m, 1 H, 2 H from **9d**), 4.69–4.73 (m, 0.5 H, 1 H from **9d**), 4.91 (dd, *J*=5.4, 1.0 Hz, 1 H, **9c**), 5.06 (s, 1.5 H, 1 H from **9c** and 1 H from **9d**). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): δ=27.7, 27.8, 28.5, 28.9, 29.0, 31.7, 31.9 (**9d**), 32.0, 35.0 (**9c**), 35.6 (**9c**), 36.9, 38.0, 38.9, 38.9, 39.8, 41.3 (**9d**), 43.8 (**9c**), 51.0 (**9d**), 73.0 (**9c**), 73.8 (**9d**), 101.2 (**9c**), 101.7 (**9d**), 201.3 (**9d**), 202.3 (**9c**). HRMS (TOF MS ES+): calcd for $C_{16}H_{23}O_3^{+}$ [M+H$^+$]=263.1646, found=263.1647. IR (KBr): ~*v*=1731, 1736, 2946, 2900 cm^{-1}.

(1*S*,2*R*,5*R*)-2-(1,4-dioxan-2-yl)-6,8-dioxabicyclo[3.2.1]octan-4-one (9 e). Levoglucosenone **1** (0.52 g, 4.1 mmol, 1.0 equiv.) was dissolved in a solution of 50 mL of acetonitrile with 1,4-dioxane (1.82 g, 1.76 mL, 5.0 equiv.) and TBADT (0.69 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: petroleum ether/ethylacetate 70/30), product **9e** was isolated as a transparent oil in 34% yield (0.29 g, 1.4 mmol) as a mixture of two diastereoisomers (2 : 1) following a conversion of 82% (0.1 g of Levoglucosenone was recovered within 8 hours of reaction). *Rf*=0.25 (petroleum ether/ethylacetate 50/50, revelation with Hannessian's stain). ^{1}H NMR (500.28 MHz, $CDCl_3$, 300 K): δ = 2.00–2.10 (m, 2.5 H, dia1+dia2), 2.44 (d, *J*=17.0 Hz, 0.5 H, dia2), 2.56 (dd, J=17.0, 8.4 Hz, 0.5 H, dia2), 2.58 (dd, *J*=17.0, 8.4 Hz, 1 H, dia1), 3.15 (dd, *J*=11.2, 10.0 Hz, 1 H, dia1), 3.36 (dd, *J*=11.2, 10.0 Hz, 0.5 H, dia2), 3.42–3.72 (m, 7.5 H, dia1+dia2), 3.77–3.82 (m, 4.5 H, dia1+ dia2), 4.54 (d, *J*=5.1 Hz, 0.5 H, dia2), 4.85 (d, *J*=1.5 Hz, 1 H, dia1), 4.97 (s, 1.5 H, dia1+dia2). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): δ=32.3 (dia1), 32.4 (dia2), 42.7 (dia2), 42.7 (dia1), 66.2 (dia1), 66.2 (dia2), 66.7 (dia1), 66.9 (dia2), 67.8 (dia1), 67.9 (dia2), 68.6 (dia2), 69.2 (dia1), 72.3 (dia1), 72.9

(dia2), 74.2 (dia1), 75.3 (dia2), 101.0 (dia1), 101.2 (dia2), 199.5 (dia1), 199.7 (dia2). HRMS (TOF MS ES+): calcd for $NaC_{10}H_{14}O_5^+$ [M+Na$^+$]=237.0739, found=237.0737. IR (NaCl): ~*v*=1719, 1735, 2858, 2907, 2962 cm^{-1}.

(1*S*,2*S*,5*R*)-2-(1,3-dioxolan-2-yl)-6,8-dioxabicyclo[3.2.1]octan-4-one (9 f) and **(1*S*,2*R*,5*R*)-2-(1,3-dioxolan-4-yl)-6,8-dioxabicyclo[3.2.1]octan-4-one (9g).** Levoglucosenone **1** (0.57 g, 4.5 mmol, 1.0 equiv.) was dissolved in a solution of 50 mL of acetonitrile with dioxolane (3.29 g, 3.1 mL, 5.0 equiv.) and TBADT (0.75 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: petroleum ether/ethylacetate 70/30), product **9f** and **9g** were isolated as 2/1 oil mixture in 31% yield (0.28 g, 1.4 mmol) following a conversion of 86% (0.08 g of Levoglucosenone was recovered within 8 hours of reaction). *Rf*=0.33 (petroleum ether/ethylacetate 50/50, revelation with Hannessian's stain). ^{1}H NMR (500.28 MHz, $CDCl_3$, 300 K): δ=1.85–1.92 (m, 0.25 H, 1 H from **9g** dia2), 2.08–2.17 (m, 1.5 H, 1 H from **9f** and 2 H from from **9g** dia1+dia2), 2.35 (dd, *J*=17.3*;* 1.2 Hz, 1 H, **9f**), 2.45 (dd, *J*=17.2*;* 1.1 Hz, 0.25 H, 1 H from **9g** dia1), 2.58 (dd, *J* = 17*:*3*;* 8*:*5 Hz, 1 H, **9f**), 2.62 (dd, *J*=17.2*;* 9.0 Hz, 0.25 H, 1 H from **9g** dia1), 2.67 (dd, *J*=17.2*;* 8.4 Hz, 0.25 H, 1 H from **9g** dia2), 3.42 (dd, *J*=8.3*;* 6.1 Hz, 0.25 H, 1 H from **9g** dia2), 3.56 (dd, *J*=8.1*;* 6.3 Hz, 0.25 H, 1 H from **9g** dia1), 3.73–3.83 (m, 2.5 H, 2 from **9f** and 2 H from **9g** dia1+dia2), 3.83–3.87 (m, 2.5 H, 2 H from **9f** and 2 H from **9g** dia1+dia2), 3.87–3.96 (m, 2.5 H, 2 H from **9f** and 2 H from **9g** dia1+dia2), 3.99–4.06 (m, 0.5 H, 2 H from **9g** dia1+dia2), 4.40–4.43 (m, 0.25 H, 1 H from **9g** dia1), 4.71–4.75 (m, 1.5 H, 1 H from **9f** and 2 H from **9g** dia1+dia2), 4.77–4.80 (m, 0.25 H, 1 H from **9g** dia2), 4.85 (d, *J*=6.0 Hz, 1H, **9f**), 4.90 (s, 0.25 H, 1 H from **9g** dia1), 4.91 (s, 0.25 H, 1 H from **9g** dia2), 4.95 (s, 1 H, **9f**), 4.96 (s, 0.5 H, 2 H from **9g** dia1+dia2). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): δ=31.7 (**9f**), 32.9 (**9g** dia2), 32.9 (**9g** dia1), 43.4 (**9g** dia2), 43.8 (**9g** dia1), 44.2 (**9f**), 64.8, 65.1, 67.6, 67.7, 67.8, 67.8, 67.9, 73.4 (**9f**), 73.5 (**9g** dia2), 74.3 (**9g** dia1), 75.0 (**9g** dia2), 75.9 (**9g** dia1), 95.0 (**9g** dia2), 95.0 (**9g** dia1), 100.9 (**9f**), 101.0 (**9g** dia2), 101.1 (**9g** dia1), 103.4 (**9f**), 199.1 (**9g** dia2), 199.4 (**9g** dia1), 199.5 (**9f**). HRMS (TOF MS ES+): calcd for $NaC_9H_{12}O_5^+$ [M +Na$^+$]=223.0582, found=223.0582. IR (NaCl): ~*v*=1735, 2899 cm^{-1}.

(1*S*,2*S*,5*R*)-4-oxo-6,8-dioxabicyclo[3.2.1]octane-2-carboxamide (9h). Levoglucosenone **1** (0.55 g, 4.4 mmol, 1.0 equiv.) was dissolved in 50 mL of acetonitrile with formamide (0.98 g, 0.87 mL, 5.0 equiv.) and TBADT (0.72 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: ethylacetate/methanol 95/5), product **9h** was isolated in 68% yield (0.51 g, 3.0 mmol) as a white solid following a conversion of 96% (0.02 g of Levoglucosenone is recovered within 8 hours of reaction). *Rf*=0.17 (ethylacetate/methanol 95/5, revelation with sulfuric acid). [*α*]546 nm *T*=20°C=-230 (c=0.12 in acetonitrile). mp : 104–105.5 °C. ^{1}H NMR (500.28 MHz, DMSO-d6, 300 K): δ=2.54–2.58 (m, 1 H), 2.71 (dd, *J*=16.8, 7.9 Hz, 1 H), 3.05 (d, *J*=7.9 Hz, 1 H), 3.91 (dd, *J*=7.5, 5.4 Hz, 1 H), 4.18 (dd, *J*=7.5, 0.8 Hz, 1 H), 4.98–5.03 (m, 1 H), 5.07 (s, 1 H), 7.13 (s, 1 H), 7.53 (s, 1 H). ^{13}C NMR (125.8 MHz, DMSO-d6, 300 K): δ=33.3, 46.2, 67.9, 75.2, 101.5, 173.6, 200.7. HRMS (TOF MS ES+): calcd for $C_7H_{10}NO_4^+$ [M + H$^+$]=172.0610, found=172.0608. IR (KBr): ~*v*=1685, 1737 cm^{-1}.

(1*S*,2*S*,5*R*)-2-(4-methoxybenzoyl)-6,8-dioxabicyclo[3.2.1]octan-4-one (9i). Levoglucosenone **1** (0.55 g, 4.4 mmol, 1.0 equiv.) was dissolved in 50 mL of acetonitrile with *p*-methoxybenzaldehyde (2.7 g, 2.4 mL, 5.0 equiv.) and TBADT (0.72 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel

(eluent: petroleum ether/ethylacetate 80/20), product **9i** was isolated in 36% yield (0.42 g, 1.6 mmol) as a white solid following a conversion of 73% (0.15 g of Levoglucosenone is recovered within 8 hours of reaction). *Rf*=0.65 (petroleum ether/ethylacetate 50/50, revelation with Hannessian's stain). [*α*]546 nm *T*=20°C=-369 (*c*=0.16 in acetonitrile). mp: 143–144°C. ^{1}H NMR (500.28 MHz, $CDCl_3$, 300 K): δ=2.74 (dd, *J*=16.9, 7.7 Hz, 1 H), 2.83 (qd, *J*=16.9, 1.0 Hz, 1 H), 3.88 (s, 3 H), 4.02–4.07 (m, 2 H), 4.22 (dd, *J*=7.6, 1.0 Hz, 1 H), 4.94–4.98 (m, 1 H), 5.13 (s, 1 H), 6.95–6.99 (m, 2 H), 7.87–7.92 (m, 2 H). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): δ=32.6, 47.6, 55.7, 68.1, 74.5, 101.7, 114.4, 127.7, 130.9, 164.1, 195.7, 198.1. HRMS (TOF MS ASAP+): calcd for $C_{14}H_{15}O_5$ $^{+}$ [M+H^{+}]=263.0919, found=263.0919. IR (KBr): ~*v*=1572, 1600, 1749, 2911, 2975 cm^{-1}.

(1*S*,2*S*,5*R*)-2-(3,4,5-trimethoxybenzoyl)-6,8-dioxabicyclo[3.2.1]octan-4-one (9j). Levoglucosenone **1** (0.59 g, 4.7 mmol, 1.0 equiv.) was dissolved in 50 mL of acetonitrile with 3,4,5-trimethoxybenzaldehyde (4.6 g, 5.0 equiv.) and TBADT (0.78 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: petroleum ether/ethylacetate 80/20), product **9j** was isolated in 49% yield (0.74 g, 2.3 mmol) as a yellow oil following a conversion of 49% (0.3 g of Levoglucosenone is recovered within 8 hours of reaction). *Rf*=0.29 (petroleum ether/ethylacetate 50/50, revelation with Hannessian's stain). [*α*]546 nm *T*=20°C=-355 (*c*=0.11 in acetonitrile). ^{1}H NMR (500.28 MHz, $CDCl_3$, 300 K): δ=2.73 (d, *J*=4.9 Hz, 2 H), 3.84 (s, 6 H), 3.86 (s, 3 H), 4.00 (dd, *J*=7.5, 5.2 Hz, 1 H), 4.03–4.09 (m, 1 H), 4.21 (d, *J*=7.5 Hz, 1 H), 4.92 (d, *J*=5.2 Hz, 1 H), 5.05 (s, 1 H), 7.1 (s, 2 H). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): δ=32.6, 47.8, 56.4, 60.9, 67.8, 74.3, 101.6, 106.1, 130.0, 143.2, 153.3, 196.5, 198.1. HRMS (TOF MS ASAP+): calcd for $C_{16}H_{19}O_7$ $^{+}$ [M+H^{+}]=323.1131, found=323.1133. IR (NaCl): ~*v*=1578, 1701, 1751, 2839, 2943 cm^{-1}.

(1*S*,2*S*,5*R*)-2-(2-methoxybenzoyl)-6,8-dioxabicyclo[3.2.1]octan-4-one (9k). Levoglucosenone **1** (0.56 g, 4.4 mmol, 1.0 equiv.) was dissolved in 50 mL of acetonitrile with *o*-methoxybenzaldehyde (3.0 g, 2.7 mL, 5.0 equiv.) and TBADT (0.74 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: petroleum ether/ethylacetate 70/30), product **9k** was isolated in 2% yield (0.02 g, 0.08 mmol) as a transparent oil following a conversion of 39% (0.35 g of Levoglucosenone is recovered within 8 hours of reaction). *Rf*=0.44 (petroleum ether/ethylacetate 50/50, revelation with Hannessian's stain). [*α*]546 nm *T*=20°C=-547 (*c*=0.01 in acetonitrile). ^{1}H NMR (500.28 MHz, $CDCl_3$, 300 K): δ=2.68 (dd, *J*=16.9, 8.1 Hz, 1 H), 2.99 (dd, *J*=16.9, 1.0 Hz, 1 H), 3.91 (s, 3 H), 4.02 (dd, *J*=7.3, 5.3 Hz, 1 H), 4.08–4.12 (m, 1 H), 4.14 (dd, *J*=7.3, 1.0 Hz, 1 H), 4.95 (d, *J*=5.3 Hz, 1 H), 5.10 (s, 1 H), 6.99 (d, *J*=8.4 Hz, 1 H), 7.07 (t, *J*=7.6 Hz, 1 H), 7.49–7.54 (m, 1 H), 7.75–7.79 (m, 1 H). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): δ=32.2, 52.5, 55.8, 68.1, 73.9, 101.7, 111.6, 121.7, 126.0, 131.1, 131.8, 134.4, 157.8, 198.6, 198.8. HRMS (TOF MS ES+): calcd for $NaC_{14}H_14O_5$ $^{+}$ [M+Na^{+}]=285.0739, found=285.0739. IR (NaCl): ~*v*=1603, 1739, 2911 cm^{-1}.

(1*S*,2*S*,5*R*)-2-(thiophene-2-carbonyl)-6,8-dioxabicyclo[3.2.1]octan-4-one (9l). Levoglucosenone **1** (0.52 g, 4.4 mmol, 1.0 equiv.) was dissolved in 50 mL of acetonitrile with 2-thiophenecarboxaldehyde (2.3 g, 1.9 mL, 5.0 equiv.) and TBADT (0.68 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: petroleum ether/ethylacetate 70/30), product **9l** was isolated in 34% yield (0.36 g, 1.5 mmol) as a white solid following a conversion of 42% (0.27 g of

Levoglucosenone is recovered within 8 hours of reaction). *Rf*=0.50 (petroleum ether/ethylacetate 50/50, revelation with Hannessian's stain). [*α*]546 nm *T*=20°C=312 (*c*=0.16 in acetonitrile). mp: 187–188 °C. ^{1}H NMR (500.28 MHz, DMSO-d6, 300 K): δ=2.56–2.6 (m, 1 H), 2.89 (dd, *J*=16.8, 7.6 Hz, 1 H), 3.98 (dd, *J*=7.8, 5.4 Hz, 1 H), 4.30 (d, *J*=7.6 Hz, 1 H), 4.37 (dd, *J*=7.8, 1.0 Hz, 1 H), 5.06–5.10 (m, 1 H), 5.14 (s, 1 H), 7.34 (dd, *J*=4.9, 3.8 Hz, 1 H), 8.11 (dd, *J*=4.9, 1.0 Hz, 1 H), 8.2 (dd, *J*=3.8, 1.0 Hz, 1 H). ^{13}C NMR (125.8 MHz, DMSO-d6, 300 K): δ=33.2, 49.5, 68.4, 76.2, 101.8, 129.9, 135.2, 136.6, 142.7, 192.3, 200.1. HRMS (TOF MS ES+): calcd for $NaC_{11}H_{10}O_4S^+$ [M+Na$^+$]=261.0197, found=261.0197. IR (KBr): ~*v*= 1651, 1732, 1749 cm^{-1}.

(1*S*,2*S*,5*R*)-2-(furan-2-carbonyl)-6,8-dioxabicyclo[3.2.1]octan-4-one (9m). Levoglucosenone **1** (0.56 g, 4.4 mmol, 1.0 equiv.) was dissolved in 50 mL of acetonitrile with 2-furaldehyde (2.1 g, 1.8 mL, 5.0 equiv.) and TBADT (0.74 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent: petroleum ether/ethylacetate 70/30), product **9m** was isolated in 7% yield (0.07 g, 0.3 mmol) as a white solid following a conversion of 35% (0.36 g of Levoglucosenone is recovered within 8 hours of reaction). *Rf*=0.94 (petroleum ether/ethylacetate 50/50, revelation with Hannessian's stain). [*α*]546 nm *T*=20°C=-32 (*c*=0.12 in acetonitrile). mp: 144–146°C. ^{1}H NMR (500.28 MHz, DMSO-d6, 300 K): δ=2.88 (dd, *J*=16.9, 7.7 Hz, 1 H), 3.97 (dd, *J*=7.7, 5.4 Hz, 1 H), 4.10 (d, *J*=7.8 Hz, 1 H), 4.36 (d, *J*=7.8 Hz, 1 H), 5.03–5.08 (m, 1 H), 5.13 (s, 1 H), 6.82 (dd, *J*=3.5, 1.6 Hz, 1 H), 7.70 (d, *J*=3.5 Hz, 1 H), 8.09 (d, *J*=1.0 Hz, 1 H). ^{13}C NMR (125.8 MHz, DMSO-d6, 300 K): δ=33.0, 49.3, 68.6, 75.9, 85.6, 102.0, 113.9, 120.9, 149.5, 187.6, 200.4. HRMS (TOF MS ES+): calcd for $NaC_{11}H_{10}O_5{}^+$ [M+Na$^+$]=245.0426, found=245.0424. IR (KBr): ~*v*=1384, 1567, 1747 cm^{-1}.

(1*S*,2*S*,5*R*)-2-nonanoyl-6,8-dioxabicyclo[3.2.1]octan-4-one (9n). Levoglucosenone **1** (0.52 g, 4.1 mmol, 1.0 equiv.) was dissolved in 50 mL of acetonitrile with nonylaldehyde (2.9 g, 3.5 mL, 5.0 equiv.) and TBADT (0.68 g, 0.05 equiv.). After 8 h of irradiation, the solvent was removed under reduced pressure and the crude product was purified over silica column gel (eluent : petroleum ether/ethylacetate 80/20), product **9n** was isolated in 50% yield (0.59 g, 2.2 mmol) as a transparent oil following a conversion of 50% (0.26 g of Levoglucosenone is recovered within 8 hours of reaction). *Rf*=0.76 (petroleum ether/ethylacetate 50/50, revelation with Hannessian's stain). [*α*]546 nm *T*=20°C=-103 (*c*=0.04 in acetonitrile). ^{1}H NMR (500.28 MHz, $CDCl_3$, 300 K): δ=0.87 (t, *J*=6.9 Hz, 3 H), 1.20–1.34 (m, 10 H), 1.58–1.79 (m, 2 H), 2.44–2.53 (m, 1 H), 2.58–2.69 (m,2 H), 2.83 (dd, *J*=16.8, 1.3 Hz, 1 H), 3.06 (d, *J*=8.0 Hz, 1 H), 4.05–4.11 (m, 2 H), 5.02–5.05 (m, 1 H), 5.11 (s, 1 H). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K): δ=d=14.2, 22.8, 23.8, 29.2, 29.3, 29.5, 31.9, 32.1, 40.5, 53.0, 67.9, 73.8, 101.8, 197.8, 207.1. HRMS (TOF MS ES+): calcd for $NaC_{15}H_{24}O_4{}^+$ [M+Na$^+$]=291.1572, found=291.1572. IR (NaCl): ~*v*=1465, 1742, 2824, 2853 cm^{-1}.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Key words

Asymmetric synthesis · Photocatalysis · Polyoxometalate · Radical reactions · Renewable resources

References

[1] (a) P. Gallezot, *Chem. Soc. Rev.* **2012**, *41*, 1538-1558. (b) C. O. Tuck, E. Pérez, I. Horvath, R. A. Sheldon, M. Poliakoff, *Science* **2012**, *337*, 695-699.

[2] M. De bruyn, J. Fan, V. L. Budarin, D. J. Macquarrie, L. D. Gomez, R. Simister, T. J. Farmer, W. D. Raverty, S. J. McQueen-Mason, J. H. Clark, *Energy Environ. Sci.* **2016**, *9*, 2571-2574.

[3] J. Sherwood, M. De bruyn, A. Constantinou, L. Moity, C. R. McElroy, T. J. Farmer, T. Duncan, W. Raverty, A. J. Hunt, J. H. Clark, *Chem. Commun.* **2014**, *50*, 9650-9652.

[4] (a) Y. Halpern, R. Ritter, A. Broido, *J. Org. Chem.* **1973**, *38*, 204-209. (b) J. He, M. Liu, K. Huang, T. W. Walker, C. T. Maravelias, J. A. Dumesic, G. W. Huber, *Green Chem.* **2017**, *19*, 3642-3653.

[5] (a) M. B. Comba, Y. Tsai, A. M. Sarotti, M. I. Mangione, A. G. Suárez, R. A. Spanevello, *Eur. J. Org. Chem*. **2018**, 590-604. (b) L. Awad, R. Demange, Y.-H. Zhu, P. Vogel, *Carbohydr. Res.* **2006**, *341*, 1235-1252.

[6] (a) A. M. Sarotti, M. M. Zanardi, R. A. Spanevello, A. G. Suárez, *Curr. Org. Synth.* **2012**, *9*, 439-459. For a selected example of heterocyclic adducts possessing cytostatic properties of interest for cancer therapy see: (b) Y. Tsai, C. M. Borini Etichetti, C. Di Benedetto, J. E. Girardini, F. Terra Martins, R. A. Spanevello, A. Suárez, A. M. Sarotti, *J. Org. Chem.* **2018**, *83*, 3516-3528.

[7] For application to the synthesis of furanones and butyrolactones see: (a) F. Diot-Néant, E. Rastoder, S. A. Miller, F. Allais, *ACS Sustainable Chem. Eng.* **2018**, *6*, 17284-17293. (b) G. Bonneau, A. A. M. Peru, A. L. Flourat, F. Allais, *Green Chem.* **2018**, *20*, 2455-2458.

[8] (a) N. Hoffmann, *Photochem. Photobiol. Sci.* **2012**, *11*, 1613-1641. (b) C. Michelin, N. Hoffmann, *Curr. Opin. Green Sustain. Chem.* **2018**, *10*, 40-45.

[9] (a) N. Hoffmann *Chem. Rev*. **2008**, *108*, 1052-1103. (b) T. Bach, J. P. Hehn, *Angew. Chem. Int. Ed.* **2011**, *50*, 1000-1045. (c) A. B. Beeler, Ed. Photochemistry in Organic Synthesis [Special issue]. *Chem. Rev.* **2016**, *116* (17).

[10] C. Michelin, N. Hoffmann, *ACS Catal.* **2018**, *8*, 12046-12055.
[11] (a) M. Fagnoni, D. Dondi, D. Ravelli, A. Albini, *Chem. Rev.* **2007**, *107*, 2725-2756. (b) D. Ravelli, S. Protti, M. Fagnoni, *Chem. Rev.* **2016**, *116*, 9850-9913.
[12] C. Taniellan, *Coord. Chem. Rev.* **1998**, *178-180*, 1165-1181.
[13] D. Ravelli, S. Protti, M. Fagnoni, *Acc. Chem. Res.* **2016**, *49*, 2232-2242.
[14] R. Blattner, D. M. Page, *J. Carbohydr. Chem.* **1994**, *13*, 27-36.
[15] H. Fischer, L. Radom, *Angew. Chem. Int. Ed.* **2001**, *40*, 1340-1371.
[16] S. Protti, D. Ravelli, M. Fagnoni, A. Albini, Chem. Commun. **2009**, 7351-7353.
[17] S. Yamada, M. Matsumoto, *Chem. Lett.* **1992**, *21*, 2273-2276.
[18] M. Okada, T. Fukuyama, K. Yamada, I. Ryu, D. Ravelli, M. Fagnoni, *Chem. Sci.* **2014**, *5*, 2893-2898.
[19] (a) K. Yamada, T. Fukuyama, S. Fujii, D. Ravelli, M. Fagnoni, I. Ryu, *Chem. Eur. J.* **2017**, *23*, 8615-8618. (b) D. Ravelli, M. Fagnoni, T. Fukuyama, T. Nishikawa, I. Ryu, *ACS Catal.* **2018**, *8*, 701-713. (c) G. Laudadio, Y. Deng, K. van der Wal, D. Ravelli, M. Nuño, M. Fagnoni, D. Guthrie, Y. Sun, T. Noël, *Science* **2020**, *369*, 92-96.
[20] L. Capaldo, D. Ravelli, M. Fagnoni, *Chem. Rev.* **2021**, DOI: 10.1021/acs.chemrev.1c00263
[21] B. P. Roberts, *Chem. Soc. Rev.* **1999**, *28*, 25-35.
[22] M. Ueda, A. Kitano, H. Matsubara, *Org. Biomol. Chem.* **2021**, *19*, 4775-4782.
[23] L. M. M. Mouterde, F. Allais, J. D. Stewart, *Green Chem.* **2018**, *20*, 5528-5532.
[24] In the case of the stereselective formation of compound **8** and the formation of the chiral center in position 7, the influence of an anomeric effect within the 1,3-dioxolane moiety could be discussed. Due to some conformational flexibility in such systems, the impact of an anomeric effect should be weaker than the steric effect. A. Vila, R. A. Mosquera, *Chem. Phys. Lett.* **2010**, *488*, 17-21. V. G. S. Box, *J. Mol. Model.* **2001**, *7*, 193-200. W. E. Willy, G. Binsch, E. L. Eliel, *J. Am. Chem. Soc.* **1970**, *92*, 5394-5402.
[25] B. Giese, H.-D. Beckhaus, *Angew. Chem. Int. Ed.* **1978**, *17*, 594-595.
[26] R. Hrdina, *Synthesis* **2019**, *51*, 629-642 and references cited therein.
[27] (a) L. Wanka, K. Iqbal, P. R. Schreiner, *Chem. Rev.* **2013**, *113*, 3516-3604. (b) A. Štimac, M. Šekutor, K. Mlinarić-Majerski, L. Frkanec, R. Frkanec, *Molecules* **2017**, *22*, 297 doi: 10.3390/molecules22020297.
[28] H.-B. Yang, A. Feceu, D. B. C. Martin, *ACS Catal.* **2019**, *9*, 5708-5715.
[29] Deposition numbers: 2085883 (**9i**), 2085884 (**9m**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures
[30] Deposition number: 2085885 (**9c/9d**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.
[31] M. Lusi, *Cryst. Growth Des*. **2018**, *18*, 3704-3712.
[32] S. Cherukuvada, A. Nangia, *Chem. Commun.* **2014**, *50*, 906-923.
[33] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone,

T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox. Gaussian Inc. Wallingford CT 2016.

[34] S. Canneaux, F. Bohr, E. Hénon, *J. Comp. Chem.* **2014**, *35*, 82-93.

[35] (a) C. Lefebvre, G. Rubez, H. Khartabil, J.-C. Boisson, J. Contreras-García, E. Hénon, *Phys. Chem. Chem. Phys.* **2017**, *19*, 17928-17936. (b) C. Lefebvre, H. Khartabil, J. C. Boisson, J. Contreras-García, J.-P. Piquemal, E. Hénon, *Chem Phys. Chem.* **2018**, *19*, 724-735. (c) M. Ponce-Vargas, C. Lefebvre, J.-C. Boisson, E. Hénon, *J. Chem. Inf. Model.* **2020**, *60*, 268-278. (d) J. Klein, H. Khartabil, J.-C. Boisson, J. Contreras-García, J.-P. Piquemal, E. Hénon, *J. Phys. Chem. A* **2020**, *124*, 1850-1860.

[36] E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comput. Chem.* **2019**, *40*, 2234-2241.

[37] D. G. A. Smith, L. A. Burns, A. C. Simmonett, R. M. Parrish, M. C. Schieber, R. Galvelis, P. Kraus, H. Kruse, R. Di Remigio, A. Alenaizan, A. M. James, S. Lehtola, J. P. Misiewicz, M. Scheurer, R. A. Shaw, J. B. Schriber, Y. Xie, Z. L. Glick, D. A. Sirianni, J. S. O'Brien, J. M. Waldrop, A. Kumar, E. G. Hohenstein, B. P. Pritchard, B. R. Brooks, H. F. Schaefer III, A. Yu. Sokolov, K. Patkowski, A. E. DePrince III, U. Bozkaya, R. A. King, F. A. Evangelista, J. M. Turney, T. D. Crawford, C. D. Sherrill, *J. Chem. Phys.* **2020**, *152*, 184108.

[38] Bruker, Apex3, 2016, Bruker AXS Inc., Madison, Wisconsin, USA.

[39] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2 : a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

[40] Sheldrick, G. M. SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015**, *71*, 3-8.

[41] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **2015**, *71*, 3-8.